IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Patent Application No. 09/833,078	)	Art Unit 2814
Filed April 12, 2001	)	Examiner: W. Louie
Confirmation No. 1456	)	Attorney Docket No.: 115354-00116 (formerly 45-35)
Inventors: David A. THOMPSON et al	)	
For: METHOD FOR LOCALLY MODIFYING THE EFFECTIVE BANDGAP ENERGY IN INDIUM GALLIUM ARSENIDE PHOSPHIDE (InGaAsP) QUANTUM WELL STRUCTURES	)	

DECLARATION UNDER 37 C.F.R. §1.131

Hon Commissioner for Patents
Washington, D.C. 20231

Sir:

In support of the Amendment filed concurrently herewith, to antedate *Haysom et al* as prior art against the above-captioned patent application, the undersigned Applicants hereby declare as follows.

1. The undersigned are the inventors of the invention disclosed and claimed in the above-captioned patent application.

2. The present Declaration is submitted to remove the applied *Haysom et al* reference as prior art by showing that the invention disclosed and claimed in the above-captioned patent application was actually reduced to practice before May 14, 2000.

3. All events set forth below took place in Canada, a NAFTA country.

4. An information disclosure form was submitted to McMaster University on a date before May 14, 2000. A true copy of the information disclosure form is attached hereto as Exhibit A, except that the date appearing on the document has been redacted. The information

disclosure form shows conception of the invention no later than that date, which is before May 14, 2000.

5. An embodiment falling within claim 1 of the present application was actually reduced to practice, by carrying out the method and testing the resulting device for suitability to its intended purpose, before May 14, 2000. The method as actually carried out used an InGaAsP multiple-quantum-well structure. That work and experimental data establishing the suitability of the device to its intended purpose are described in a paper entitled "Demonstration of a DFB Laser with an Integrated Electo-Absorption Modulator Produced Using a Novel Quantum-Well Intermixing Technique" by G. J. Letal, D. A. Thompson, B. J. Robinson, and J. G. Simmons. A draft of the paper prepared before May 14, 2000, is attached hereto as Exhibit B.

6. The co-author J. G. Simmons did not contribute to the conception of the invention and is not a co-inventor of the present claimed invention. He was the co-supervisor of the student G. J. Letal, who is a named inventor, and is named as a co-author only in that capacity. He had no role in the quantum well intermixing using the LT- and He-plasma InP or in the conception of the invention in general.

7. An embodiment falling within claim 12 of the present application was actually reduced to practice, by carrying out the method and testing the resulting device for suitability to its intended purpose, before May 14, 2000. That work and experimental data establishing the suitability of the device to its intended purpose are described in a paper entitled "Enhanced band-gap blue shift by low-temperature grown InP in InGaAsP multiple quantum-well laser structures," by A. S. W. Lee, D. A. Thompson, and B. J. Robinson. A draft of the paper prepared before May 14, 2000, is attached hereto as Exhibit C.

We further declare that all statements made of our own knowledge are true and that all statements made on information and belief are believed to be true; and that all statements are made with the knowledge that willful false statements and the like are punishable by fine or imprisonment, or both (18 U.S.C. §1001) and may jeopardize the validity of the application or any patent issuing thereon.

Respectfully submitted,

D. A. Th
David A. Thompson

7 March 2003
Date

Brad Robinson
Bradley J. Robinson

Mar 7 2003
Date

Gregory Letal
Gregory J Letal

March 10, 2003
Date

Alex S. W. Lee

Mar 7, 2003
Date

115354.00116/35312738v1

McMaster University

INVENTION DISCLOSURE FORM

I. DESCRIPTION.

Invention Title: New methods for locally modifying the effective bandgap energy in indium gallium arsenide phosphide (InGaAsP) quantum well semiconductor device structures.

Description: Several methods exist for changing and/or controlling the effective bandgap energy in quantum well structures that rely on methods of locally inducing controlled inter-diffusion between the quantum wells and adjacent barrier regions. Reported methods rely on impurity induced inter-diffusion, impurity-free inter-diffusion (via ion implantation plus thermal anneal or capping the structure with a deposited dielectric, such as silicon dioxide, plus thermal anneal) or laser annealing. Each of these methods has problems associated with surface contamination, uniformity, reproducibility or strain effects. The invention described in this disclosure overcomes most of these problems and introduces a new phenomenon that can impact on the high speed performance of some devices. This invention uses specially grown indium phosphide (InP) layers that are used to implement the bandgap energy control. These layers are grown in-situ in a molecular beam epitaxy chamber eliminating interfacial and surface contamination effects. Then, using conventional photolithographic patterning and subsequent thermal anneal treatments, local area quantum well/barrier inter-diffusion can be implemented.
Two methods of growing the relevant InP layers are described:

(1) growth of the InP layer at normal growth temperatures whilst subjecting the growing surface to a continuous helium plasma stream generated with an electron cyclotron resonance source. This layer then contains a high concentration of specific defects that diffuse through the quantum well-barrier region during a subsequent thermal anneal treatment, causing controlled inter-diffusion and a controllable change in the effective bandgap energy. The defects formed during this growth process have been demonstrated to dramatically decrease the carrier lifetime in InP and InGaAsP such that when they are quenched into the quantum well region any subsequently processed device would be expected to exhibit ultra-fast response.

(2) growth of the InP layer at a temperature considerably lower than the normal growth temperature. This layer also contains a high concentration of specific defects, but different to (1) above, that diffuse through the quantum well-barrier region during a subsequent thermal anneal treatment, causing controlled inter-diffusion and a controllable change in the effective bandgap energy. While this method does not have potential for high speed devices it can be implemented at a somewhat lower anneal temperature which is important when fabricating integrated opto-electronic devices involving lasers where the laser wavelength is normally modified by the anneal step.

Applications: Integrated opto-electronics, e.g. laser with integrated modulator (possible very high speed with helium plasma grown InP), laser with integrated low loss waveguide, integrated waveguide and photo-detector, tunable wavelength lasers.

Advantages: Inherently strain-free and, free of interfacial and surface contamination problems, highly controllable growth of the InP layer in a molecular beam epitaxy chamber (the active layer in the process is grown as part of the device structure without need to remove the structure from the high vacuum environment of the epitaxy chamber).

Current status of work: Work is continuing and there is room for optimization and calibration of the process. An example of the application of a distributed feedback laser with an integrated electro-absorption modulator has been demonstrated employing the helium plasma

grown InP. Optimization of the device design and fabrication process still needs to be carried out as does testing of the high speed performance of the modulator section.

II. PUBLICATIONS, PUBLIC USE AND SALE.

A. Two abstracts to conferences to be held in May and July, 2000 have been submitted. Details attached.

B. We plan to write a Letter for publication of the low growth temperature InP in the near future. G Letal (graduate student) is close to submitting his PhD thesis which will describe the use of the helium plasma InP and the demonstration device.

C. Details of the helium plasma InP and InGaAsP growth have been given in several papers but the application to modification of the effective bandgap of quantum well structures has not been reported.

D. There have been extensive articles published on the techniques of ion implantation and anneal, impurity diffusion, dielectric capping and anneal, and laser annealing as techniques for achieving local effective bandgap modification.

III. SPONSORSHIP.

Materials and Manufacturing Ontario under the project entitled "Growth, Fabrication and Characterization of Distributed Feedback Lasers with Enhanced Performance"

IV. PARTICIPANTS.

David A. Thompson, Professor, Department of Engineering Physics, McMaster University.
Brad. J. Robinson, Research Engineer, CEMD, McMaster University.
Gregory J. Letal, Graduate Student, Department of Engineering Physics, McMaster University.
Alex S. W. Lee, Postdoctoral Fellow, CEMD, McMaster University.

V. OWNERSHIP.

Dr David A. Thompson **(30%)**, 5 Birch Crescent, Greensville, Ontario, L9H 6A6.
Dr Brad J. Robinson **(30%)**, 109 Balmoral Ave. South, Hamilton, Ontario, L8M 3K1.
Gregory J. Letal **(30%)**, 76 Mericourt Road, Apt #2, Hamilton, Ontario, L8S 2N9.
Dr Alex S. W. Lee **(10%)**, 5 Glenmount Ave., Hamilton, Ontario, L8S 2L3.

Brad Robinson
Gregory Letal

I/We have read and understand our rights and obligations under McMaster University's Intellectual Property Policy. Specifically I/We understand that under that Policy we have the right to ask for an assignment of the Intellectual Property to be made to us (Section 11). This will confirm that we have decided **to/not to** (delete as applicable) take such an assignment.

Inventors:

D. A. T

Brad Robinson

Gregory Letal

DEMONSTRATION OF A DFB LASER WITH AN INTEGRATED ELECTRO-ABSORPTION MODULATOR PRODUCED USING A NOVEL QUANTUM-WELL INTERMIXING TECHNIQUE

G.J. Letal, D.A. Thompson, B.J. Robinson, and J.G. Simmons

Centre for Electrophotonic Materials and Devices, McMaster University, Hamilton, ON. Canada. L8S 4L7
Phone:(905)525-9140x24932 fax:(905)527-8409 email:dathomp@mcmaster.ca

Abstract

Bandgap engineering is used extensively in the telecommunications field. Quantum well intermixing (QWI) is a post-growth method of bandgap engineering that has been studied for the integration of photonic devices.[1] A novel method of QWI has been discovered which uses layers of indium phosphide grown by helium-plasma-assisted gas source molecular beam epitaxy, subsequently referred to as He*-InP, in combination with thermally induced QWI. The He*-InP has been shown to contain large numbers of defects which can act as fast non-radiative recombination centres[5] . These can be used with the thermally-induced QWI to produce regions with a larger band-gap and containing the fast, non-radiative defect centres. This novel intermixing process has been used to fabricate integrated distributed feedback (DFB) lasers and electro-absorption (EA) modulators.

Introduction

The semiconductor industry is currently interested in integrating various optoelectronic devices, such as lasers, waveguides, modulators, and detectors on a single wafer. Post-growth band gap modification of selected areas of a quantum well (QW) structure is one technique by which this can accomplished[1]. Typical methods being investigated are: dielectric-enhanced intermixing[2], ion implantation[3], laser induced intermixing[1], and low-temperature grown GaAs induced intermixing[4]. Each method involves the generation and diffusion of defects which are used to selectively intermix quantum wells and adjacent barriers. Dielectric enhanced intermixing uses a dielectric cap (usually SiO_2) and a subsequent rapid thermal anneal (RTA) to produce enhanced quantum well intermixing (QWI) in the capped, relative to the uncapped regions[2]. Ion implantation followed by a RTA produces enhanced QWI in the implanted regions[3] and laser induced disordering uses localized heating to produce regions of enhanced QWI[1]. Alternatively, the gallium vacancies found in low-temperature-grown GaAs can intermix GaAs-type quantum well structures[4]. Dielectric-enhanced intermixing has experienced much interest due to its relative simplicity of implementation as compared to ion implantation or laser-induced intermixing. However, for InP-based structures we have identified problems associated with MBE growth over regions that have experienced dielectric-enhanced QWI, thereby making it difficult to use for the integration of certain types of devices.

We have developed a novel method of QWI which exploits the defects found in layers of indium phosphide grown by helium-plasma assisted gas source molecular beam epitaxy (GSMBE) to fabricate integrated DFB lasers and EA modulators. Layers of He*-InP have previously been shown to contain significant numbers of vacancy-type defects (presumably P-vacancies) that produce levels deep within the bandgap causing the material to have a very short carrier lifetime[5]. Unlike dielectric-enhanced intermixing, re-growth problems can be overcome. This paper discusses how these defects can be incorporated in thermally induced QWI regions to produce an EA modulator, containing fast recombination centres, integrated with a DFB laser.

He*-InP Induced Intermixing

In a GSMBE grown multiple QW structure with a top cladding layer of InP and an InGaAs contact layer, QWI can be induced by a simple RTA process. The defects responsible are either grown-in in the cladding and contact layers or are generated at the surface. These defects are fast diffusers and since, in our case, the barrier and QW layers have identical group III compositions, we can speculate they are diffusing as group V interstitials. If a sufficiently thin He*-InP layer is inserted between the upper quaternary guiding and cladding layers, this layer will trap some of the diffusing interstitial defects. However, it also supplies some slow diffusing vacancy defects to the active region to enhance the QWI process whilst increasing the recombination rate in the EA modulator section. The result is an increased bandgap in the EA region together with deep levels that quench the photoluminescence (PL) and reduce the carrier lifetime. Clearly, the thickness of the He*-InP layer

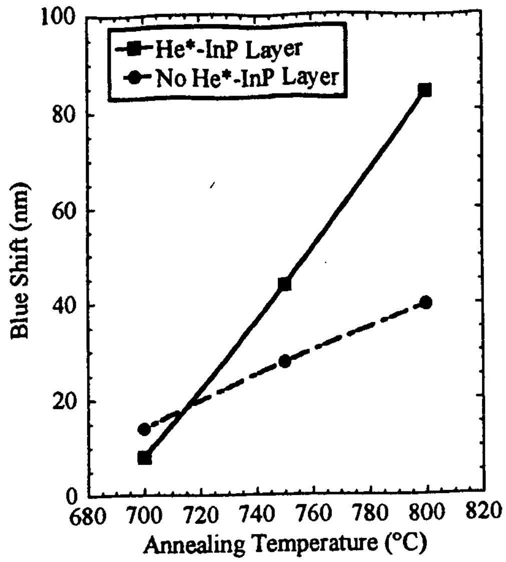


Fig. 1: Quantum well intermixing for a sample with and without a He*-InP layer. (30s anneals)

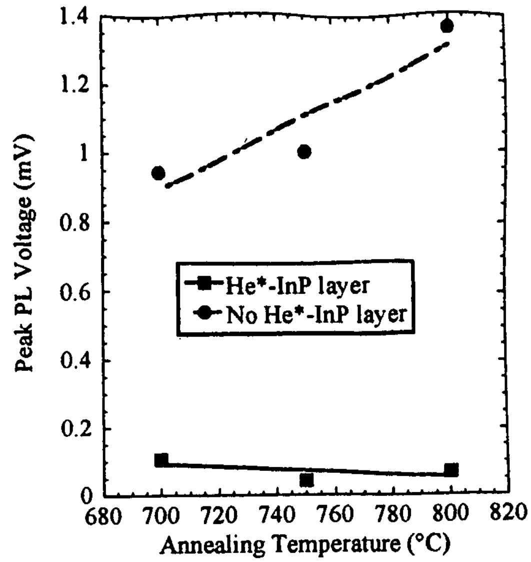


Fig. 2: Variation of PL peak voltage with annealing temperature for samples with and without He*-InP layers (30s anneal)

has to be sufficient to supply enough deep states to the active region whilst allowing enough interstitials to reach the active region and produce QWI so the EA modulator region is transparent at zero bias. If it is too thick QWI is completely suppressed. Why?

A typical intermixing result for a 40nm He*-InP layer grown directly on the quaternary waveguide layer is illustrated in Figs. 1 and 2 (measured using low-temperature-photoluminescence, LTPL, since there is no measurable room-temperature PL signal for the samples with the He*-InP layer). (The error in the PL intensity measurement is ±10%.) For a 30s, 800°C anneal, a sample with the He*-InP experienced a 44nm(±2nm) greater blue-shift than a sample with a normal InP layer, and the PL was reduced by approximately a factor of 30. This reduction in the PL intensity suggests the presence of non-radiative defects in the QW region. Future work is required to confirm that these defects are the optically fast defects observed in He-plasma grown MBE InP[5].

Re-growth Over Annealed Material

From a processing standpoint, it is desirable to carry out the QWI step before etching the grating and completion of the laser growth. The re-growth interface can have an unpredictable effect on the intermixing process and the PL can be measured after the intermixing for the partially grown laser structure, unlike a completed laser structure where material absorption makes the PL measurement difficult. Also, the grating can be matched to the PL peak if there is change in the QW wavelength in the laser pump region due to the anneal treatment.

In our research on integrating various devices using oxide-enhanced, quantum well intermixing, defect-free re-growths could not be achieved using MBE. Typically the surface of the re-growth layer had a rough morphology, particularly over the regions subjected to enhanced QWI. This was due to the propagation of interface defects, and could not be eliminated even with a 7000Å thick sacrificial layer separating the re-growth interface from the oxide cap layer. However, QWI using the He*-InP layers with only a 1500Å layer of sacrificial InP can produce sufficient QW modification without the associated re-growth problems. This ability to re-grow over He*-InP intermixed regions is motivation for developing the He*-InP defect induced intermixing technique. If the sacrificial layer is chemically removed after the anneal, standard re-growth procedures (as developed by Robinson et al.[6]) can be followed to obtain a re-growth of comparable quality to that over an un-annealed structure.

Device Fabrication

Integrated DFB lasers and EA modulators were fabricated using thermal QWI with He*-InP in the modulator section. The devices were based on a 3-quantum-well ridge-waveguide (RWG) laser. A schematic diagram of the completed device structure is illustrated in Fig. 3. The processing procedure is discussed in detail elsewhere[7], but a summary is provided here.

Device fabrication was complicated by the fact that the He*-InP defect has a short diffusion length, and that 1500Å of material is required to protect the

Å = 1x10^-10 m 150nm

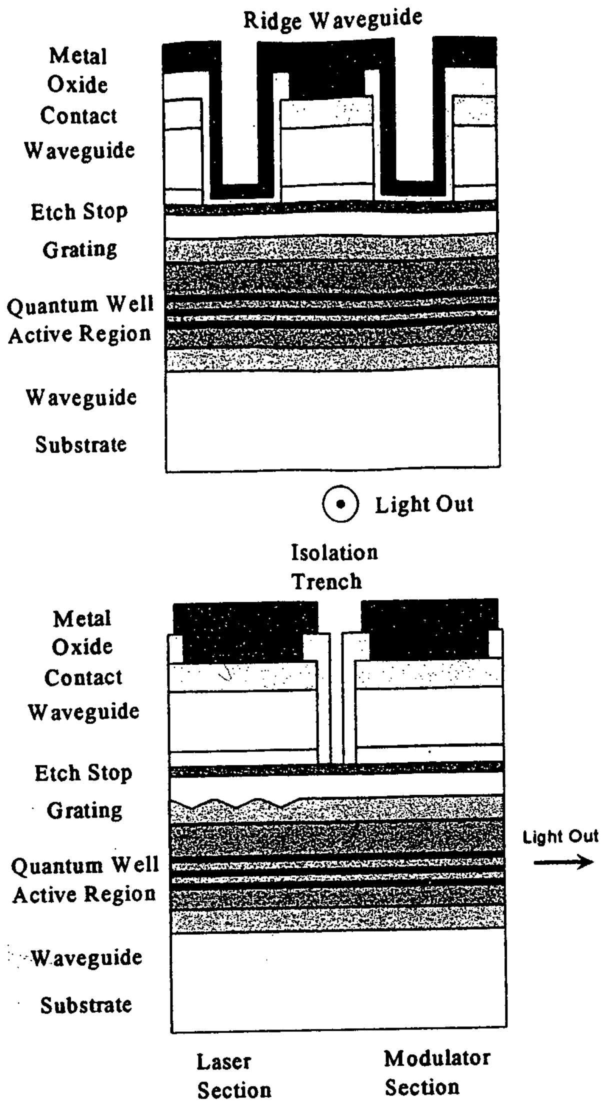


Fig. 3: Schematic diagram of the fabricated device.

surface during anneal. Because of this, two re-growths are required when fabricating the integrated device: one to grow the sacrificial layers required for the anneal and for patterning the grating; and one to grow the top waveguide and contact layers. (The He*-InP layer was grown during the first growth). Even though two re-growths were required, a process was developed so that only one additional mask step was necessary over that required for the fabrication of a regular DFB laser. This was accomplished by using a He*-InP layer to both induce the intermixing and to act as an etch mask to inhibit grating formation in the modulator section during the grating patterning step. (An etch mask was required to inhibit grating formation in the modulator section because the grating was patterned using a holographic system.)

Standard selective etches* were used to remove the etch mask before the re-growth

Device Results

Integrated DFB lasers and EA modulators based on a 3-quantum-well ridge-waveguide (RWG) laser structure were fabricated by using the He*-InP defect induced intermixing technique. The He*-InP layer was 70nm thick which provided a 29nm relative blue-shift between the modulator and laser section. For this thickness of He*-InP, the PL was reduced by approximately a factor of 50.The ridge width of the different devices ranged from 2 to 4μm. The isolation trench width was varied from 5 to 15μm. The resistance between the top contacts varied between 2 and 20kΩ, depending on the width of the trench. The modulator differential resistance was measured to be 10kΩ, which means that the leakage current between the laser and modulator will form a significant fraction of the total modulator current. Still, the isolation is sufficient to illustrate the principle of the device. Optical coupling is estimated at between 40 and 60% depending on the device geometry. (Larger ridge widths have a larger coupling between the devices.)

The fabricated DFB lasers had threshold currents ranging from 18 to 35mA, depending on ridge width. The L-I curves were linear, and free of mode hopping up to a maximum measured input current of 100mA. The emission wavelength of the devices were 1568, 1570, and 1572nm for a 2, 3, and 4μm RW respectively.

The modulator showed no measurable electroluminescence up to the maximum forward bias current of 100mA. This result suggests that the dominant transition in the modulator section is now a non-radiative transition, since even a poorly operating (i.e. non-lasing) laser structure will emit measurable spontaneous emission at an input current of 100mA.

The change in absorption at the emission wavelength as a function of modulator bias (i.e. the extinction ratio) was measured for an integrated device. A typical result for a 400μm long modulator with 2μm RW is illustrated in Fig. 4. This graph shows an 11.8dB reduction in the intensity of light measured from the modulator facet when a 3V bias is applied. The extinction ratio varied with ridge-width due to the different modal indices (and therefore different lasing wavelengths) of the devices. This extinction ratio illustrated in Fig. 4 is sufficient for many device applications.

---

* 1:8:80 H_2SO_4:H_2O_2 for InGaAs, and 1:3 HCL:H_3PO_4 for InP.

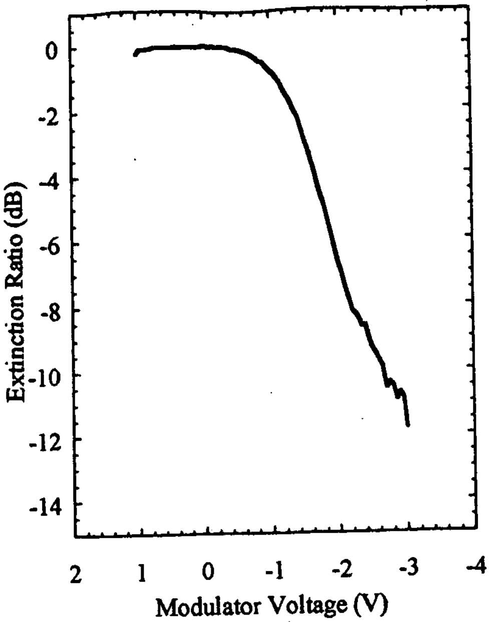


Fig. 4: Variation of the modulator extinction ratio with modulator voltage

The operating voltage of 3V can be reduced in future designs by optimizing the position of the absorption edge relative to the emission wavelength, and to further optimize the modulator design. The extinction ratio under modulation still needs to be measured.

Modulator facet feedback was a problem for the integrated devices with 3 and 4μm ridge widths since the facets were not antireflection (AR) coated. This effect exhibited itself as mode hops in the device output spectrum and as a non-linear L-I curve. Modulator facet reflectivity was a lesser problem for the 2μm devices since the optical coupling between the laser and the modulator was relatively poor. Future work will investigate the effects of applying AR coatings to the modulator facets of the devices.

Summary

Integrated DFB lasers and EA modulators have been fabricated using the novel technique of He*-InP defect induced intermixing, thereby proving the technique's feasibility for fabricating integrated devices. This intermixing technique allows for re-growths over 800°C annealed material, which provides a major advantage over dielectric-enhanced intermixing. A 70nm layer of He*-InP provided a 29nm relative blue-shift between the laser and modulator sections. Electroluminescence and photoluminescence measurements both suggest that the EA modulator material has a reduced carrier lifetime due to the introduction of non-radiative defects into the QW region (though the magnitude of the reduction has yet to be determined). It is hoped that this technique can be used to integrate fast QW devices with standard QW devices.

1) J. H. Marsh, O. P. Kowalski, S. D. MacDougall, B. C. Qiu, A. McKee, C. J. Hamilton, R. M. De La Rue and A. C. Bryce, J. Vac. Sci. Technol. A, **16**, (1998) 810.
2) N. Cao, B. B. Elenkrig, J. G. Simmons and D. A. Thompson, Appl. Phys. Letts., **70**, (1998) 3419.
3) S. Charbonneau, E. Koteles, P. Poole, J. He, G. C. Aers, J. Haysom, M. Buchanan, Y. Feng, A. Delage, F. Yang, M. Davies, R. Goldberg, P. Piva and I. V. Mitchell, IEEE J. Sel. Topics in Quantum Electronics, **4**, (1998) 772.
4) J. S. Tsang, C. P. Lee, S. H. Lee, K. L. Tsai and J. C. Fan, J. Appl. Phys., **79**, (1996) 664.
5) H. Pinkney, D. A. Thompson, B. J. Robinson, P. Mascher, P. Simpson, U. Myler, J. U. Kang and M. Frankel. J. Vac. Sci. Technol. A, **16**, (1998) 772.
6) B. J. Robinson, J. Bursik, D. A. Thompson, G. C. Weatherly and R. W. Streater, Proc. IPRM'99, Davos, IEEE Catalog #99CH36362, (1999) 135.
7) Letal, G.J., "Integrated distributed feedback lasers and electroabsorption modulators fabricated using helium-plasma-assisted InP defect induced quantum well intermixing", Ph.D Thesis, McMaster University, 2000.

Enhanced band-gap blue shift by low-temperature grown InP in InGaAsP multiple quantum-well laser structures.

A. S. W. Lee, D. A. Thompson and B. J. Robinson

Center for Electrophotonic Materials and Devices, McMaster University, Hamilton, Ontario L8S 4L7, Canada

Abstract:

Quantum well intermixing (QWI) in an InGaAsP multiple quantum-well (MQW) laser structures is demonstrated using an InP epitaxial layer grown at 300 °C, by gas source molecular beam epitaxy (GSMBE), followed by rapid thermal annealing (RTA). Photoluminescence (PL) is used to compare the magnitude of the QWI process between low temperature (LT) and normal temperature (NT, 470 °C) grown InP layers as a function of both anneal temperature and time. For example, after an anneal at 780 °C, a large band-gap blue-shift of ~197 nm is observed in MQW structures capped with LT-InP as compared to an ~35 nm shift in identical structures capped with NT-InP. Also, the effect of the LT-InP capping is compared to NT-InP, capped with a dielectric (~1000 Å of SiO_2), following anneal at 800 °C for 60 s. This shows blue-shifts of ~243 nm and ~142 nm respectively.

Quantum well intermixing (QWI) has attracted considerable interest recently for locally modifying the QW band structure and in device applications such as tunable wavelength lasers,[1] photodetectors,[2] modulators,[3] and optoelectronic integrated circuits.[4] Different thermally-driven intermixing techniques, such as ion-implantation disordering (IID),[5] impurity-free defect diffusion (IFDD),[6] laser-induced methods of which photo-absorption induced disordering (PAID) appears most attractive,[7] and impurity-induced layer disordering (IILD),[8] have been utilized to modify the QW structure in selected regions. However, all of these techniques have their advantages and disadvantages. In IID, for example, the high energy implanted ions may introduce lattice damage to the QW structure that cannot be annealed and consequently result in reduced light output. The IILD technique, though simple, may require long anneal times and/or high anneal temperature (> 800 °C).[9] It also introduces unwanted impurities. IFDD is free of impurities, but control of the QWI process depends on the deposited dielectric cap layer being used, it's deposition conditions and the subsequent thermal anneal treatment. Also, strain and damage may be introduced at the hetero-structure surface.[10] A problem with PAID may be it's poor spatial resolution[11].

A simple, clean, and easy technique that can achieve large band-gap blue-shift in the InP-based materials system under moderate anneal conditions has been developed. In this letter, we report the first large band-gap blue-shift in a 1.55μm InGaAsP MQW laser structure induced by low temperature (LT) grown InP. A large wavelength blue-shift of >>100nm is demonstrated using LT-InP grown at 300 °C and subsequent anneals at 600-780 °C for various times.

The MQW structure is shown in Fig. 1. It consists of a truncated laser growth that is terminated with additional thin InP and InGaAs layers immediately above the upper quaternary guiding layer. The 250 Å InP layer is used in the etching of a grating for the fabrication of a distributed feedback (DFB) laser. The 1000 Å InP layer is either LT-InP or

InP grown at normal temperature (NT) for determining the relative effects of the LT-InP in the QWI process. This is separated from the lower InP layer with a 50 Å InGaAs etch-stop layer. The whole structure is then capped with 1000 Å of InGaAs which may or may not be removed prior to anneal. The samples used in these experiments were grown by GSMBE at a rate of 1μm/hr on n-type (001) InP substrates. Group V constituent atoms are supplied in the form of As_2 and P_2 derived from the pyrolysis of AsH_3 and PH_3 in a single, two zone low pressure cracker with a Ta catalyst operating at 1000 °C. All layers were grown at 470 °C with the group V total flow rate of 4 or 5 sccm except the top most 0.1 μm InP layer, which was grown either at 300 °C (LT) or at normal temperature, 470 °C (NT). It is relevant to note that the In/Ga ratios in the QW and barrier layers are identical, only the group V compositions were different. The anneals were carried out under a flowing nitrogen ambient using a halogen lamp rapid thermal annealing (RTA) system (AG Associates, Mini-Pulse 610). For comparison with the dielectric-enhanced IFDD process some samples with the NT-InP were capped with approximately 1000 Å of SiO_2 deposited using plasma-enhanced chemical vapor deposition (PECVD) at 300 °C. All samples were covered with an InP substrate to protect the surface and minimize phosphorus evaporation during the RTA treatment. The anneals were carried out in the temperature range of 600 - 800 °C for different time intervals between 5 and 150 s. The quantum well emission wavelength was determined by room temperature photoluminescence (PL) using the 488 nm line of an argon ion laser as the excitation source.

Figure 2 shows the PL results for both LT and NT InP samples annealed at 600 – 780 °C temperatures for 30 s. A larger blue-shift is evidenced for the LT grown InP (with or without InGaAs shield) as compared to the NT InP sample for all anneal temperatures. A large wavelength shift of ~197 nm is induced by the LT grown InP layer at 780 °C whereas only an ~35 nm blue-shift is observed for the NT InP. The large band-gap blue-shift is due to

the abundance of point defects in the LT grown InP layer. These have been postulated to be donor-like P-antisites[12] or acceptor-like In-vacancies[13]; i.e. the layer is P-rich[14]. As the annealing proceeds, these point defects diffuse to the QW region and enhance the intermixing effects between barrier and quantum well materials.

Note that for LT InP, the wavelength blue-shift is almost identical, but possibly slightly higher, for the samples with the InGaAs shield layer on. However, this is not the case for NT-InP samples at temperature between 650 to 750 °C where samples with the InGaAs shield layer show a significantly larger blue-shift. For the NT-InP structure it appears that grown-in defects generate the observed blue-shift at the higher anneal temperatures. Then, the additional blue-shift for anneals between 650 to 750 °C in the sample with the InGaAs shield may be due to grown-in defects in the shield layer which become mobile at 650 °C and depleted at about ~700 °C. Then defects in the InP cladding and InGaAsP active region become mobile above ~700 °C and dominate at temperatures >750 °C.

Figure 3 shows the results of PL measurements of both the LT- and NT-InP samples, with the InGaAs shield etched off, annealed at 725 °C as a function of anneal time. Both samples exhibit initial large blue-shifts for anneals of only 5 s. However, the LT-InP sample gives an ~71 nm blue-shift which is more than double that of the NT InP sample. For longer anneals the NT-InP shows a steady increase in blue-shift with time of ~0.07 nm/s while the blue-shift for the LT-InP rises much more rapidly to ~173 nm wavelength shift at 150 s. The shape of the blue-shift versus anneal time suggests a saturation effect occurs, possibly as the source of defects is exhausted. This is under study.

Figure 4 shows the PL spectra of LT- and NT-InP samples annealed at 800 °C. The NT-InP samples were annealed with or without a SiO_2 cap. As can be seen from the figure, the NT InP sample is blue shifted ~57 nm after 60 s, with enhanced PL intensity and narrower FWHM, as compared to the as-grown sample. The dielectric capped NT-InP

samples exhibited a blue-shift of ~142 nm after 60 s and ~214 nm after 180s, while the PL intensity after 60s is greater than the as-grown sample but the FWHM is increasing with time. The LT-InP sample annealed for 60 s exhibits ~243 nm band-gap shift, considerably larger than the dielectric capped sample after anneal for 180 s.

In summary, we report a new technique to induce large band-gap blue-shifts in InGaAsP/InP MQW laser structures using a layer of LT-grown InP. A large net wavelength blue-shift of ~197 nm is exhibited by this technique when the sample is annealed at 780 °C for 30 s. This epitaxial technique is intrinsically clean and free of interface impurities, strain and plasma damage that may occur in the dielectric-capped IFDD technique, and as a consequence we expect improved reproducibility in the blue-shift due to the elimination of impurities, interfacial strain and damage due to the PECVD process. Also, larger blue-shifts are obtained with the LT-InP compared to the IFDD process with the same anneal conditions. This means it should be possible to achieve blue-shifts, for say a DFB/integrated electro-absorption modulator at a sufficiently low anneal temperature that the process does not significantly shift the wavelength in the laser section from the as-grown wavelength.

This work is supported by Materials and Manufacturing Ontario, a Provincial Centre of Excellence.

References

1. N. Cao, B. B. Elenkrig, J. G. Simmons, D. A. Thompson, and N. Puetz, *Appl. Phys. Lett.* **70**, 3419 (1997).
2. A. S. W. Lee, E. H. Li, and Gamani Karunasiri, *Appl. Phys. Lett.* **74**, 1102 (1999).
3. S. J. Lycett, A. J. Dewdney, M. Ghisoni, C. E. Norman, R. Murray, D. Sansom, J. S. Roberts, *J. Electron. Mater.* **24**, 197 (1995).
4. E. H. Li, *Quantum Well Mixing and Optoelectronic Device Applications*, Milestone Series, vol. 145, Bellingham, WA: SPIE Press, 1998.
5. P. Chen and A. J. Steckl, *J. Appl. Phys.* **77**, 5616 (1995).
6. Shu Yuan, Yong Kim, C. Jagadish, P. T. Burke, M. Gal, J. Zou, D. Q. Cai, D. J. H. Cockayne, and R. M. Cohen, *Appl. Phys. Lett.* **70**, 1269 (1997).
7. B. S. Ooi, C. J. Hamilton, K. McIlvaney, A. C. Bryce, R. M. De La Rue, J. H. Marsh and J. S. Roberts, *IEEE Photonics Technology Letters* **9**, 587 (1997).
8. Y. T. Oh, S. K. Kim, T. W. Kang, C. Y. Hong, and T. W. Kim, *J. Appl. Phys.* **77**, 2415 (995).
9. Y. T. Oh, S. K. Kim, T. W. Kang, C. Y. Hong, and T. W. Kim, *J. Appl. Phys.* **77**, 2415 (995)..
10. J. H. Marsh, *Semicond. Sci. Technol.* **8**, 1136 (1993).
11. A. McKee, G. Lullo, C. J. McLean, B. C. Qiu, A. C. Bryce, R. M. DeLaRue, and J. H. Marsh, 1997 Conf. on Indium Phosphide and Related Materials, Hyannis, MA. IEEE Catalog #97CH36058, p288-291.
12. P. Dreszer, W. M. Chen, K. Seendripu, J. A. Wolk, W. Walukiewicz, B. W. Liang, C. W. Tu, and E. R. Weber, *Phys. Rev. B* **47**, 4111 (1993).
13. P. Hautojärvi, J. Mäkinen, S. Palko, and K. Saarinen, *Mat. Sci. Eng.* B **22**, 16 (1993).

14. K.Xie, C. R. Wie and G. W. Wicks, MRS Proc. **241**, 265 (1992).

Figure Caption

Fig.1. Schematic diagram of the InGaAsP/InP MQW structure used in this study.

Fig.2. The photoluminescence peak wavelength shifts of both the LT and NT grown InP samples annealed for 30 s as a function of temperature.

Fig.3. The photoluminescence peak wavelength shifts as a function of annealed time for both the LT and NT grown InP samples annealed at 725 °C.

Fig.4. Room temperature photoluminescence spectra of both the LT and NT grown InP samples annealed at 800 °C. Some of the samples are capped with ~1000 Å SiO_2 before annealing, as indicated in the figure.

1000 Å	InGaAs	$p = 1 \times 10^{18}$
1000 Å	InP	$p = 1 \times 10^{18}$
50 Å	InGaAs	$p = 5 \times 10^{17}$
250 Å	InP	$p = 6 \times 10^{17}$
800 Å	1.15 Q	$p = 5 \times 10^{17}$
700 Å	1.24 Q	undoped
50 Å	QW	undoped
100 Å	1.24 Q	undoped
50 Å	QW	undoped
100 Å	1.24 Q	undoped
50 Å	QW	undoped
700 Å	1.24 Q	undoped
800 Å	1.15 Q	$n = 5 \times 10^{17}$
5000 Å	InP	$n = 1 \times 10^{18}$
	n^{+} InP Substrate	

Fig. 1

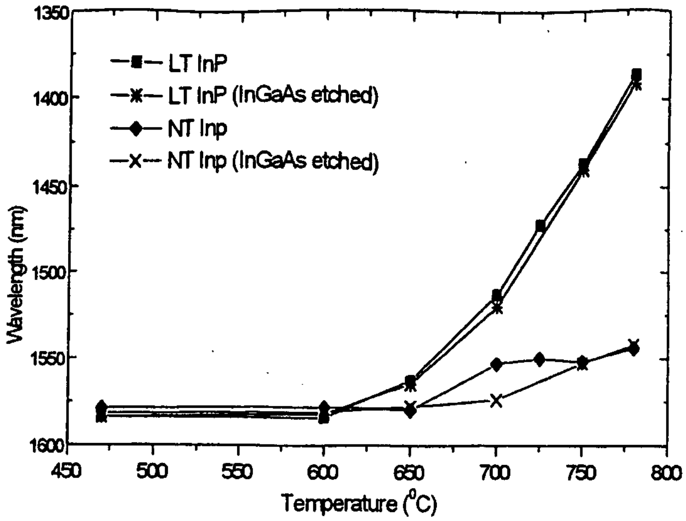
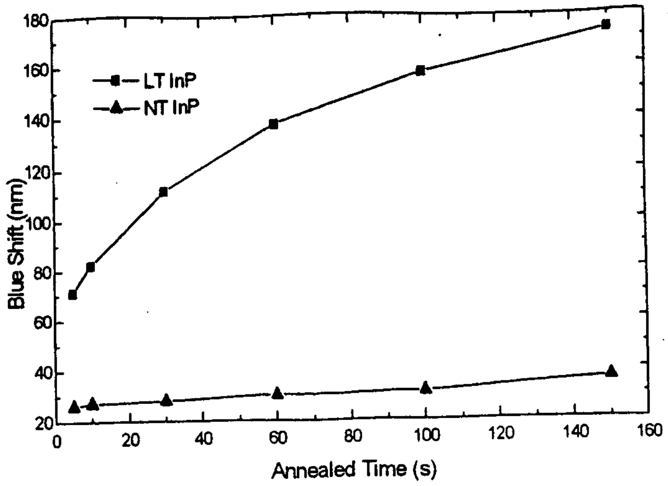

1350
1400
1450
1500
1550
1600
450
500
550
600
650
700
750
800
Wavelength (nm)
Temperature (°C)
LT InP
LT InP (InGaAs etched)
NT Inp
NT Inp (InGaAs etched)

Fig. 2



LT InP
NT InP
Blue Shift (nm)
Annealed Time (s)
180
160
140
120
100
80
60
40
20
0
20
40
60
80
100
120
140
160

Fig.3

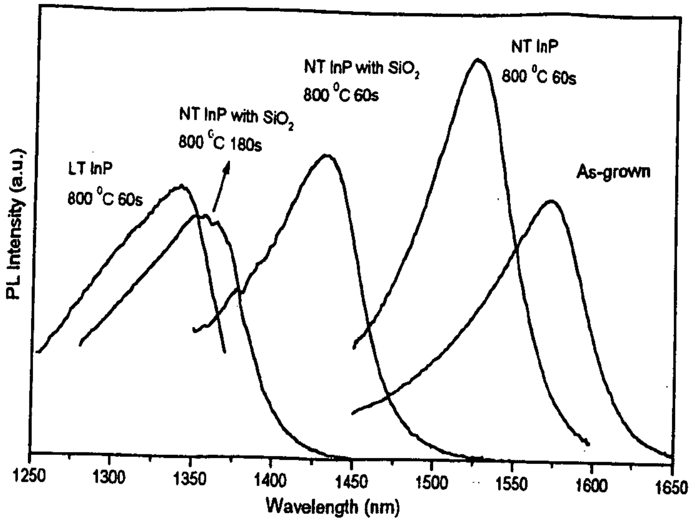

NT InP
800 °C 60s
NT InP with SiO2
800 °C 60s
NT InP with SiO2
800 °C 180s
LT InP
800 °C 60s
As-grown
PL Intensity (a.u.)
1250
1300
1350
1400
1450
1500
1550
1600
1650
Wavelength (nm)

Fig. 4